

Implementing infrared determination of quartz particulates on novel filters for a prototype dust monitor

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Research by the National Institute for Occupational Safety and Health (NIOSH) has pursued quartz analysis for the specialized filter assemblies of a new worker-wearable personal dust monitor (PDM). The PDM is a real-time instrument utilizing a tapered element oscillating microbalance (TEOM®). Standard fiberglass TEOM filters cannot accommodate the desired P-7 infrared analytical method used by the Mine Safety and Health Administration (MSHA). Novel filter materials were tested with the objective of demonstrating this type of analysis. Low temperature ashing and spectrometric examination were employed, revealing that nylon fiber candidate filters left minimal residual ash and produced no significant spectral interference. Avoiding titanium dioxide in all filter materials proved to be a key requirement. Fine quartz particulates were collected on prototype filters in a Marple chamber, either open-faced or through PDMs during test runs. The filters were then subjected to MSHA P-7 analysis and the spectrometrically based analytical results for quartz mass were compared to reference measurements. Also, PDM instrumental mass readings were compared to filter gravimetric measurements. Results suggest that the P-7 method is adaptable to variations in filter materials and that quartz dust analysis by the P-7 method when utilizing the new ashable PDM filters can have accuracy and precision within 10% and 4%, respectively. This is within the declared 13% accuracy and 7–10% precision of the P-7 method itself. Instrument mass readings had modest positive bias but met NIOSH accuracy criteria. Continued work with specialized PDM filters is merited, as they are a new type of TEOM sample amenable to ashing analysis of particulates.

1. Introduction

1.1 Background

Coal worker's pneumoconiosis and silicosis remain ongoing concerns for the coal mining industry's workforce.¹ The risk of lung disease increases with the extent of dust exposure. Higher exposures to crystalline silica (hereafter called quartz) may be a factor in the rapid progression of coal-related pneumoconiosis to more serious stages, as well as the cause of silicosis.² The concentration and the composition of airborne particulate matter present in coal mining environments are both points of regulatory concern. Collecting airborne dust samples and determining their quartz content has been integral to measuring miner exposure to mine dust and demonstrating compliance with US Federal regulations.³

The established regulatory method for quantifying exposure to coal dust employs person-wearable pumps to draw samples through cyclones onto membrane filters. At a time and location

distant from the sampling, the filters are gravimetrically and spectrometrically analyzed. Then, with knowledge of the air volume drawn, coal and quartz dust exposures are calculated. In 1996, the US Secretary of Labor commissioned an advisory committee to study ways of preventing pneumoconiosis among coal mine workers. The committee recommended⁴ development of dust monitoring instruments capable of providing more timely exposure information directly to miners. Consequently, the National Institute for Occupational Safety and Health (NIOSH) and the Mine Safety and Health Administration (MSHA) began development of a continuous real-time dust monitor. In consultation with labor, industry, and government, NIOSH issued a contract (no. 200-98-8004) to Rupprecht and Patashnick Co., Albany, NY, now part of Thermo Fisher Scientific, Inc., Waltham, MA (hereafter termed Thermo). Going beyond past efforts,⁵ the research involved miniaturizing tapered element oscillating microbalance (TEOM®) technology into a continuous and worker-wearable personal dust monitor (PDM). The PDM constituted a promising new instrument, but it had no means to accommodate quartz analysis of dust samples. As part of its research with PDMs, NIOSH sought to achieve quantitative quartz analysis of dust collected on PDM filter assemblies.

MSHA annually performs about 20 000 quartz analyses of coal mine dust samples that have been collected on polyvinyl-chloride (PVC) membrane filters. PDM filter assemblies, however, are inherently different from PVC membranes in their structure, composition, and mass. While current filter assemblies are mechanically and physically suitable for their instrumental

application, the standard assembly formulation is completely unamenable to quartz analysis, in that it contains some very durable materials that cannot be ashed.

Preparatory ashing of PVC filter samples destroys organic materials that contribute to their mass, both from collected coal dust and the filters themselves. The spectral properties of the simpler sample matrix (*i.e.*, residual ash) are less complex than for the original sample. Interferences with the intended analyte, quartz, are substantially reduced and the accuracy of analysis is improved. It is particularly necessary to ash PDM filter assemblies before analysis because their opacity entirely impairs transmission spectrometric examination of samples. Also, removal of collected dust for separate analysis is not viable, because the removal would not be quantitatively reliable. Therefore, ashing PDM samples is a requirement before analysis, but no filter assembly formulation existed that could successfully accommodate an ashing procedure.

1.2 The PDM, filters, and analytical requirements

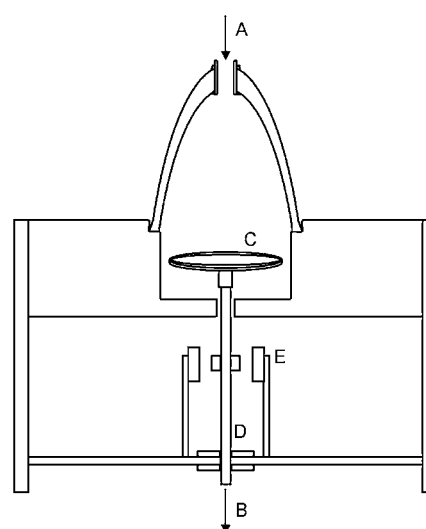
TEOMs have found varied applications⁶ in environmental monitoring and particulate measurement. Details on TEOM principles^{7,8} and PDM operation⁹ are available elsewhere. Performance of the new TEOM-based PDM has been documented by NIOSH researchers through extensive testing,¹⁰ evaluating its accuracy as comparable to gravimetric samplers. Only those technical points on the PDM most relevant to this research are reviewed here.

The battery powered PDM is a combined dust monitor and cap lamp, similar in size and weight (3.0 kg) to traditional battery packs used for miners' cap lamps. A sampling run is initiated either with buttons on its faceplate or with a personal computer and a specialized program. The faceplate has a display for continuous data readout, but downloading the PDM's stored electronic data file requires a personal computer and instrument software.

The instrument has a brass inlet attached to the side of the cap lamp, which is within the worker's breathing zone. A conductive silicone rubber tube (0.48 cm id, 152 cm length) is used to draw particulate-laden air at 2.2 L min⁻¹ from the inlet to the instrument. This tube has been shown not to cause significant loss of respirable size particulates.¹¹ At the external tube's junction with the instrument main body, a cyclone size-fractionates the particulates and transmits the respirable portion of a sample through heated zones inside the PDM. Heating the air sample establishes a steady state temperature, stabilizing instrument performance and reducing the influence of humidity on mass readings.

At the end of the instrument's internal sampling train is the miniaturized TEOM, where dust is collected on an attached filter assembly. Discussion of PDM filters in this article refers to complete filter assemblies, unless the context indicates the fibrous filtration material is the topic. PDM filters mount directly on the tapered element, which is a very narrow steel tube. Fig. 1 presents a schematic of the TEOM with a mounted PDM filter.

PDM instruments utilize a specialized filter assembly that is constructed from three sonically welded components. The largest component is a circular polypropylene (PP) base with a hollow axial stem, which frictionally attaches to the exposed end of the



Key:

- A – Sampling Airflow Inlet
- B – Sampling Airflow Outlet
- C – Filter Assembly
- D – Tapered Element Tube
- E – Vibration Electronic Feedback Elements

Fig. 1 Schematic of the PDM TEOM with a filter mounted.

tapered element. The second component is a small fibrous filter mat which rests on the PP base. Dust deposits on the 14 mm diameter filter mat, while a pump draws air through it *via* the tapered element tube. The final component is a PP ring, used to seal the rim of the filter mat onto the base. These components (further described below) are assembled by the manufacturer, with the end user's activity usually limited to mounting and removing filter assemblies from the tapered element with a special tool.

The dust samples MSHA currently analyzes for quartz are deposited on 37 mm diameter, 5.0 μ m pore, PVC membrane filters, collected using sealed plastic cassettes. MSHA employs its P-7 method of analysis,¹² which involves ashing the PVC sample filters and redepositing the ash onto PVC-acrylic copolymer membrane filters, by means of an isopropanol suspension. The redeposited samples are then examined in a Fourier transform infrared spectrometer. Through calibration-based calculations, the spectrometer output is used to quantify the mass of quartz in the samples after correction for kaolin clay, a common interferent that may be found in coal dust. As mentioned earlier, other interferences are reduced by the ashing step of the method.

In contrast to PVC membranes, the fibrous filter mat Thermo normally uses for PDMs (as well as 1400-series TEOMs) is EMFAB™ TX40H120WW (Pallflex Products Corp., Putnam, CT, part of Pall Corp., East Hills, NY). This high efficiency filter mat contains three particularly rugged materials. The filter medium is composed of random borosilicate fiberglass, with a polytetrafluoroethylene (PTFE) polymer binder, cured at over 370 °C. Also, a layer of woven glass fabric is incorporated as a structural backing. This composition for the filter mat is thoroughly unashable, particularly with a low temperature asher, the usual means of destroying organics in quartz analysis of coal mine samples and the sole asher type employed in this study.

Therefore, a reformulated filter material for unashable fiberglass was needed, close to 100% organic, of nonshedding fibrous construction, and with high dust loading capacity. High loading capacity is necessary, because several mg of mine dust may be collected on the small filter mat. PDM filters have only 18% of the dust collection surface of PVC filters (collection diameters: 14 mm vs. 33 mm). The new filter material also had to be as efficient in particle collection as the current EMFAB, but without excessive pressure drop.

The PP components of the PDM filter constitute a mechanical frame with their own potential to be problematic in ashing procedures. Their mass is much greater than that of a membrane filter. The mass of a ring/base set (one ring plus one base) ranges from 90–100 mg (105–115 mg with a filter mat), while PVC membranes range from 12–15 mg. While PP items could, in theory, be ashed as thoroughly as an organic membrane filter, there is no previous experience with how long ashing these heavier, thicker components might require. If the time is longer than a day, ashing could be impractical. Furthermore, in that fillers and additives are typically a portion of polymer formulations, any mineral added to the PP could frustrate the analytical goal.

There are currently two compositional variations for the PP components: white (the dominant variation in the past) and clear. The white components are tinted, for cosmetic reasons, with 0.5% titanium dioxide (TiO_2) pigment. They also contain other inorganic-bearing additives, such as antioxidants and pH neutralizers, composing no more than another 0.2%. Therefore, the mean total mass of a white ring/base set being 97.9 mg, the expectable inorganic portion may be up to 0.685 mg. The clear components contain no colorant and only the maximum 0.2% noncolorant additives. The mean total mass of a clear ring/base set being 91.8 mg, 0.184 mg would be their expectable maximum inorganic mass.

The possibilities for interference from these significant amounts of inorganic material seem great. TiO_2 is a mineral that will not ash and so it could interfere with the infrared absorbance bands of other minerals. However, substantial amounts of ash remain after coal dust is processed in an asher, without impairing the spectrometric analysis. Therefore, the spectral properties of an ash appear to be more important than the mass. If quartz quantitation is to be achieved with PDM filters, then it is necessary to demonstrate that some PP variation has an interference-free ash, including when combined with a suitable ashable filter mat. Trial PDM filter assemblies that met the above criteria needed to be fabricated and tested in actual quartz determinations, with the goal of examining them as replacements for the existing PDM filter.

2. Experimental procedures

2.1 Initial ashing and dispersion tests

Four sets of PP components for PDM filters, two ring/base sets each of white and clear PP, were ashed (asher model LTA-504, LFE Corp., Clinton, MA) to determine if their ashing time was acceptable and if their residue would disperse in isopropanol. These PP components are the highest mass items incorporated into a PDM filter assembly. As such, they are the most difficult to

ash. Successful ashing and dispersion of the PP components would suggest successful processing of complete filter assemblies, because the much lighter filter mats would be of minor extra consequence in the ashing process. Settings for the asher were those typical for ashing membrane filters, and no specific adjustments were made for these samples. After the samples developed a stable appearance, they were removed from the asher at 0.5 h intervals and weighed to track mass loss with longer ashing time.

Although the PDM uses internal heating to control the influence of humidity, an inherently hydrophobic filter can still be helpful. PTFE and Reemay® polymer were once mentioned^{5a} as possible choices for TEOM filters, because of presumed hydrophobicity. In a separate test, a 25 mm diameter, 1–2 μm pore, PTFE filter (catalogue no. 12009-M-1132, Berghof/America, Coral Springs, FL) was cut into pieces and weighed. The pieces were subjected to extended times in an asher and checked for mass loss. Reemay polyester filter material (Fiberweb, PLC, Nashville, TN) was not available with a filtration efficiency meeting implementation requirements for PDM filters and thus was eliminated as a possibility.

2.2 Spectrometric evaluation of candidate filter assembly materials

In investigating spectral interference, a market search was conducted for candidate filter materials to replace Pallflex EMFAB. Some compromises were made in the earlier discussed criteria, to keep the range of products tested from being too few or too similar. Although they have uncertain filtration efficiency, specialty cellulose filters were included because of their reputation for low ash. PP electret filters were included because of their general versatility, although they can shed fibers and their electrostatic properties can cause weighing instability.

Squares of the candidate filter materials were cut, roughly 12–13 mm on each side, to approximately match the area of the PDM filter mat. PP components were also included in these tests, being parts in current PDM filter assembly construction. PVC and PVC-acrylic membranes, filters used in the P-7 method, were included as reference materials for comparison.

All samples were ashed and the sample residues taken to MSHA's Dust Division laboratory for P-7 processing. MSHA performed sample dispersion in isopropanol, redeposition onto PVC-acrylic filters, and analysis using a Perkin Elmer Spectrum™ 2000 Fourier transform infrared spectrometer with version 2.00 Spectrum software. To enhance signal-to-noise and spectral detail, these initial analyses utilized 64 scans at 4 cm^{-1} resolution, while subsequent P-7 analyses used the more typical 1 scan at 8 cm^{-1} resolution. All analyses used 1 cm^{-1} as the spectrum data point interval setting.

2.3 Differential pressure and filtration efficiency evaluation

Differential pressure of selected filter materials was briefly examined across 10 mm diameter samples mounted in Swinnex® threaded holders (catalogue no. SX0001300, Millipore Corp., Billerica, MA). An airflow rate of 2.2 L min^{-1} was used, matching the airflow of PDMs, and differential pressure was measured with a digital pressure gage (model 370, Setra Systems, Inc.,

Boxborough, MA). Readings were then normalized to a hypothetical sample diameter of 14 mm, the actual PDM filter mat size, by multiplying by the ratio of filter areas (*i.e.*, 0.5). Manufacturer specifications for filtration efficiencies were also obtained.

2.4 Quartz analysis with open-face collected samples

Guided by the evaluation of candidate materials, prototype PDM filter assemblies were fabricated using both polyester- and cellulose-back nylon fiber mats mounted in clear PP components. Particulate collection from air suspension was used to introduce controlled masses of quartz onto these filters for trial analyses. A direct open-face collection method was tried first as the simplest approach to generate test samples. Using prototype PDMs for quartz collection was reserved for subsequent tests. Certain plastic tube connectors (catalogue nos. E-06458-10, -20, and -30, Cole-Parmer Instrument Co., Vernon Hills, IL) were found to provide airtight seals when the stems of PDM filters were inserted in their 2 mm diameter orifices, confirmed by the retention of an applied vacuum to plugged filter assemblies. As illustrated in Fig. 2, devices utilizing the connectors were assembled for the open-face particulate collection tests.

Two test runs were performed in a Marple chamber (ELPRAM Systems Inc., Minneapolis, MN), using Minusil®-5 dust (US Silica Co., Berkeley Springs, WV). To generate a dust source, the chamber utilizes a model 3400 fluidized bed aerosol generator and model 3012 charge neutralizer (TSI, Inc., St. Paul, MN). Each run consisted of five polyester-back PDM filters and five cellulose-back PDM filters, arranged in a circle, collecting synchronous parallel samples. The chamber's rotating turntable served to accomplish spatial averaging of the test atmosphere. Escort® Elf pumps (Mine Safety Appliances Co., Pittsburgh, PA) drew air at 2.2 L min^{-1} , turned on and off simultaneously in each test. A Thermo model 1400a TEOM was used to monitor each

experiment and help achieve target masses of approximately $500 \mu\text{g}$ per sample. This quartz mass is in the linear range of the P-7 method and high enough to help reduce error levels for both gravimetric and spectrometric analysis.

Throughout this research, Marple chamber tests ran for specified times, either 1 or 2 h. Dust feed rates into the chamber were controlled to achieve the target collected masses in the specified time spans. Airborne Minusil-5 concentration ranged $2\text{--}4 \text{ mg m}^{-3}$. Temperature was maintained at $20\text{--}25^\circ\text{C}$ and relative humidity maintained at $40\text{--}60\%$. All samples were oriented face down during sampling and chamber airflow proceeded (less than 10 cm min^{-1}) from top to bottom. Above the PDM filters were aluminium foil cowls (disposable weighing pans) to prevent the settling mode of dust collection. This arrangement (Fig. 2) ensured that dust mass on the filters was from air sampling and not gravity-caused settling onto nonfilter surfaces. This avoided the possibility of dust loss from nonfilter surfaces during filter assembly handling.

Weights of the filter prototypes tended to drift readily if rigorous procedures were not followed. To avoid this, pre- and post-dust collection weighings were performed with careful attention to humidity and electrostatic influences. Before each stage of weighing, samples were equilibrated for at least 2 days in an environmentally controlled balance room, maintained at 22°C and 52% relative humidity. Each type of prototype filter had two balance room reference samples, whose mean inter-day weight changes were used to apply a weight correction. Electrostatic elimination was performed with each filter sample for a period of 3 min, between two model 2U500 static eliminator strips (NRD, Inc., Grand Island, NY), one beneath and another above the sample.

Post-weighed filters were deposited directly in the clean glass beakers that would be used for ashing. The beakers were then transported to MSHA for treatment in an ashers (model 600, Anatech USA, Hayward CA), isopropanol redeposition, and spectrometric analysis. This experiment would determine if spectrometric analysis and gravimetric analysis produced the same assessments for the quartz mass in each sample.

The spectrometric procedure of the P-7 analysis was performed twice on each ashed sample. The analysis requires that a background reference spectrum be subtracted from the spectrum of a sample. Typically, the spectrum of a blank PVC-acrylic filter is the background subtracted. In this current research, one procedure variation retained subtraction of a PVC-acrylic filter; the second variation employed subtraction of an ashed PDM filter that had been redeposited onto a PVC-acrylic filter. This would reveal whether fully matching spectral references to samples was of analytical importance.

Another test was necessary for correct evaluation of quartz analysis with the prototype filters. This was a more direct spectrometric analysis of the particular Minusil-5 source material, by the same P-7 technique that would be applied to the filter samples. Because the Minusil-5 dust was unlikely to be perfectly crystalline and pure, it had to be determined how the P-7 method would assess it. For calibration purposes, the P-7 method currently uses Standard Reference Material (SRM) 1878A (National Institute for Standards and Technology, Gaithersburg, MD), a material available only in very limited quantities. It is therefore unworkable to use SRM 1878A in a Marple chamber

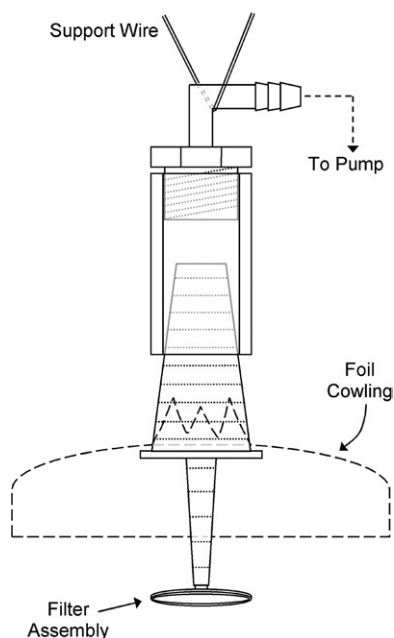


Fig. 2 Apparatus used for collecting Minusil-5 dust on PDM filters.

to generate test atmospheres, and the more abundant Minusil-5 was used instead. Minusil-5 and SRM 1878A are similar, but not identical, materials high in quartz. A source material comparison analysis would provide a correction factor for the minor differences between them and require only small samples for the tests. By isopropanol dispersion, four 300 μg samples each of Minusil-5 and SRM 1878A were deposited on PVC-acrylic filters, followed by spectrometric analysis.

2.5 Quartz and mass analyses with PDM-collected samples

In another series of tests, Minusil-5 was collected onto prototype filters while mounted in PDMs during sampling runs. The same Marple chamber, dust generating device, conditions and procedures for the initial dust collection tests were used here as well. Each filter composition separately underwent six tests, with each test employing three prototype PDM units and four cyclone samplers interspersed in a circle, all synchronously operated in parallel and drawing air at 2.2 L min⁻¹. The performance of the Higgins-Dewell cyclones (model BGI4CP, BGI, Inc., Waltham, MA) used in this experiment match that of the cyclone in the PDM design. They are able to accept tubing inlets and were fitted here with tubes of the same length as the PDMs. The cyclones collected samples onto 37 mm diameter, 5.0 μm pore, PVC filters, which served as comparison references for the PDM filters. Balance room procedures for gravimetric assessment of PDM filters matched those used earlier, but with expanded sets of six reference filters. The static elimination period for PVC filters was 1 min, known to be sufficient for membranes. PDM and PVC filters were ashed in separate groups, for respectively appropriate times.

This experiment would determine if PDM and cyclone sampling systems would produce the same P-7 measurements for quartz when run side-by-side. Both sets of samples collected the same dust (of the same crystallinity) assessed by the same technique. This made a crystallinity-related correction factor derived from source dust analysis inapplicable in this case. A PVC-acrylic filter spectrum was used as the reference in these analyses, guided by work with ashed PDM filter references, which showed no clear benefit for background spectrum subtraction. Comparisons were also performed between gravimetric assessments of collected mass for the two filter sets, as well as between PDM instrument mass readings and gravimetric data. These comparisons would examine PDM mass measurement accuracy when using the prototype filter assemblies. All statistical calculations for bias, precision, accuracy, and accuracy upper confidence limit (UCL) were derived from the procedures and equations of Kennedy *et al.*¹³

2.6 Particle sizing tests

During the PDM tests, the particle size distribution of airborne Minusil-5 was also briefly examined by use of Thermo model SE298 Marple cascade impactors. The impactors were operated at 2.0 L min⁻¹, with eight stages above a final filter, having cutpoints from 0.52 to 21.3 μm . In two separate trials, an impactor collected suspended particulates during the course of two tests run on the same day, ensuring sufficient dust mass for gravimetric accuracy.

3. Results

3.1 Results of initial ashing and dispersion tests

Residue of the PP components had stable visual appearance after about 5.5 h of ashing. There was no further significant mass loss after 6.5–7 h. While PVC filters typically ash in 1–1.5 h, it appears that roughly 7 h is required to ash PDM samples. It was decided, however, to ash PDM samples for at least 10 h in subsequent experiments, simply to ensure that the older ashers available for the research completed their task. The results with PP indicated that ashing PDM samples can be achieved within a day. As expected, white components left much more visible ash than clear components. However, both types of ash dispersed in isopropanol with only brief agitation in an ultrasonic bath. The completed ashing process produced fine powder residues free of polymer that might act as a binder. This indicated that the redeposition step of the P-7 procedure could be applied to complete PDM filter assemblies.

For the PTFE filter pieces tested, 1.8% mass loss resulted from 6 h ashing and 3.6% loss resulted from 12 h. At this ashing rate, approximately 14 days would be needed for full filter destruction, an impractical time period for large scale analyses. Consequently, PTFE was eliminated from consideration in any new filter design.

3.2 Results of spectrometric evaluation of candidate filter assembly materials

Most samples left minimal ashing residue and all dispersed in isopropanol, with brief ultrasonic agitation. PVC-acrylic and PVC filters, the comparison references, showed minimal false readings for both kaolin and quartz. The quartz limit of quantitation (LOQ) for PVC membranes was calculated as $\sim 7 \mu\text{g}$. While work with coal dust on PVC field samples has an LOQ of 20 μg (the stated LOQ for the P-7 method),¹² a 7–10 μg LOQ is achievable when handling only pure quartz. Bearing in mind that detection and quantitation limits¹⁴ for quartz are dependent on the specific matrix and method employed, the PVC-related $\sim 7 \mu\text{g}$ LOQ estimate agrees with other P-7 experience. None of the materials tested showed large false readings for kaolin. However, some of the materials might not allow an adequately low LOQ for quartz. White PP ring/base sets and a spun bound cover for electret filters caused significant negative quartz readings. Both contain TiO₂, proving concerns that it might act as an interferent. (Table A-1 in the ESI records detailed results from P-7 analysis of the tested samples.†)

Fig. 3 shows infrared spectrum traces of ashed white and clear PP ring/base sets that were included in this evaluation, illustrating how TiO₂ is a problem. The ashed clear PP produced a relatively featureless spectrum. However, the white PP produced a very broad and strong infrared absorbance spanning roughly 850–450 cm⁻¹, comparable to spectra in the literature,¹⁵ caused by TiO₂ in the ash. In the P-7 method, a kaolin peak is measured 930–900 cm⁻¹, an area not greatly affected by TiO₂ absorbance. However, both a kaolin peak and a quartz doublet are measured 815–770 cm⁻¹, which is on the TiO₂ absorbance shoulder. A straight baseline drawn across this region results in a false “negative absorbance” from the gap between the baseline and the spectrum trace curving a little under it. The curvature of

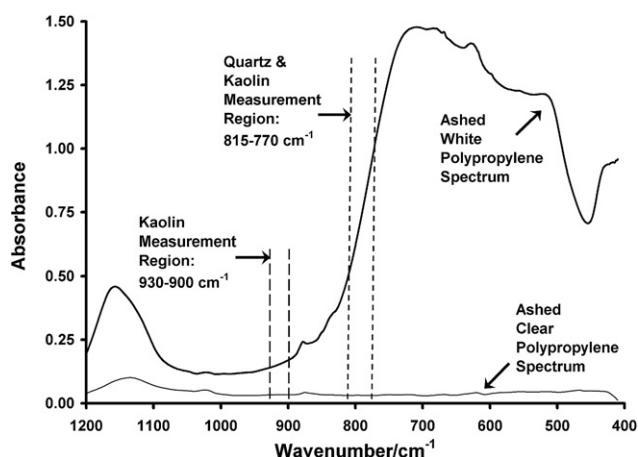


Fig. 3 Comparison of infrared spectra of ashed white and clear polypropylene.

the TiO_2 shoulder introduces a negative bias into the quartz measurement. Consequently, white PP filter components are found to be unsuitable for quartz analysis, but clear PP components are found to be suitable.

Several TiO_2 -free materials showed acceptable spectrometric performance after ashing. Their estimated quartz LOQ was within the desirable $20\text{ }\mu\text{g}$ limit for P-7 field samples. This would be the case even when the effects of the filter mat and clear PP components are combined, as they would be for an actual filter assembly. Of the samples spectrometrically tested, a HEPA nylon fiber filter material was the most promising. When joined with clear PP components, the resultant LOQ would likely not exceed $\sim 10\text{ }\mu\text{g}$ quartz ($\sim 7\text{ }\mu\text{g}$ from the filter mat, plus $\sim 3\text{ }\mu\text{g}$ from the clear PP). This is in the current P-7 LOQ range when examining pure quartz.

3.3 Results of differential pressure and filtration efficiency evaluation

Differential pressure contributions to the test apparatus from standard fiberglass and HEPA nylon filters were essentially the same, $1.7\text{--}1.9\text{ kPa}$ ($13\text{--}14\text{ mm Hg}$). PDMs are designed for pressure drops up to 16.7 kPa (125 mm Hg), so both filter materials permit heavy dust samples with large differential pressures without exceeding this limit. Also, specified filtration efficiency of the HEPA nylon fiber candidate material was similar to that of the standard fiberglass filter. Both the fiberglass and nylon materials exceed 99% collection efficiency with $0.3\text{ }\mu\text{m}$ diameter dioctylphthalate particles. While other materials might be workable, HEPA nylon filters were the best current match for the full set of desired properties. Thus, the research continued, using two variations of HEPA nylon filter that had either cellulose or polyester support backings (Pallflex materials N1840 and N1841, respectively).

3.4 Results of quartz analysis with open-face collected samples

P-7 source material analysis assessed Minusil-5 samples at 0.942 times their gravimetrically determined masses. The SRM 1878A samples (precisely matching the calibration standard) did not show this difference. The Minusil-5 source dust may be expected

to produce P-7 quartz mass determinations 5.8% less than corresponding gravimetric values. This needed correction likely derives from the Minusil-5 being a little lower in actual quartz content than SRM 1878A.

There was high quartz recovery for the open-face samples and minimal mean difference between actual and expected P-7 determinations, within about 1% for both PDM filter types. Also, while they may be adopted as a point in careful analytical procedure, ashed PDM filters as spectral references did not show a clear benefit in these tests. (Table A-2 in the ESI records detailed results of the open-face PDM filter tests.†)

3.5 Results of quartz and mass analyses with PDM-collected samples

P-7 quartz analyses for both of the PDM filter types had mean agreement with the reference PVC sample analyses within 1–2%. This side-by-side comparison examined only spectrometric quartz measurements independent of gravimetry. For the gravimetric comparisons, the mean agreement between PVC samples and the two types of PDM filters was within 2–3%. PDM-assessed end-of-file (EOF) dust masses, the final instrument mass reading from each test file for prototype filters, had 5–7% mean higher values compared to PVC gravimetric data. EOF measurements also had mean higher values compared to polyester- and cellulose-back filter gravimetric measurements by 4% and 8%, respectively. In this last comparison, polyester-back filters produced better PDM instrument agreement. (Table A-3 in the ESI records detailed spectrometric results for the PDM-collection tests; Tables A-4 and A-5 give detailed gravimetric results.†)

Table 1 lists summary statistics for the comparisons performed with data from the PDM tests. Individual measurements are compared to mean reference results; subscript M denotes the mean of the sample type indicated. The statistical results for the PDM-collection tests are reported for each of the two compositions of PDM prototype filter and for each PDM unit. Tabular entries include bias, precision, accuracy, and accuracy 95% UCL. The accuracy UCL can be compared with NIOSH criteria for accuracy of measurement methodologies, which require it be no more than 25%. It was found subsequent to the tests that the PDM no. 3 TEOM was not correctly calibrated. The unit also failed to operate in one test. Therefore, PDM no. 3 EOF readings were not included in the data sets, but other data types from this PDM unit were included.

Because of the modest size of the data sets, accuracy and other statistics in Table 1 (and other tables) cannot be taken as final quantitative assessments of analytical performance. However, useful indications of performance are still available from the various data analyses. It is noted that accuracy 95% UCLs are all less than 25%, the key NIOSH accuracy criterion. Noteworthy are the UCL values, close to the 25% limit, for cellulose-back filter EOF data compared to PDM filter gravimetric data. This reflects the less desirable bias and accuracy entries for that specific data comparison. For all calculated statistics in that category of comparison, polyester-back filters performed better than cellulose-back filters. Focusing only on polyester-back filters, Table 1 records quartz analysis accuracy within 10% and precision within 4% for compared P-7 analyses of PDM filters

Table 1 Statistical summary for all data comparisons from PDM-collection tests^{a,b}

Comparison type	PDM no.	Polyester-back filter results (%)				Cellulose-back filter results (%)			
		Bias	Precision	Accuracy	Acc. 95% UCL	Bias	Precision	Accuracy	Acc. 95% UCL
PDM P-7/PVC _M P-7	1	−1.6	4.0	8.8	16.8	−2.1	2.0	5.9	10.7
	2	0.6	0.7	2.8	5.4	0.1	0.1	2.5	4.7
	3	−4.1	3.1	9.5	17.9	−1.7	2.1	5.7	10.6
PDM grav./PVC _M grav.	1	2.9	1.9	6.4	10.8	−2.5	3.6	8.8	16.7
	2	3.6	1.5	6.4	10.0	−1.2	2.4	5.8	11.1
	3	0.3	2.5	5.2	10.9	−2.4	1.7	5.8	10.2
PDM EOF/PVC _M grav.	1	5.6	2.2	9.4	14.2	4.6	3.2	10.2	17.2
	2	7.6	2.0	11.2	15.8	7.0	2.4	11.4	16.9
PDM EOF/PDM _M grav.	1	3.0	0.4	5.2	7.9	6.8	4.4	14.3	23.6
	2	5.0	2.3	9.2	14.6	9.3	4.1	16.2	24.8

^a Subscript M denotes the mean of the sample type indicated. ^b PDM no. 3 EOF data was not included; related statistics were not calculated.

and reference PVC filters. This is within the declared 13% accuracy and 7–10% precision of the P-7 method itself. Accuracy calculations for polyester-back filters in Table 1 are within ~11% for all comparisons performed. Positive biases are recorded for EOF comparisons to PVC and polyester-back filter gravimetric data, ranging within 3–8%.

3.6 Results of particle sizing tests

Results from the two trials were consistent, with mass median aerodynamic diameters of 2.33 and 2.28 μm and geometric standard deviations of 1.75 and 1.74. This confirmed that most of the Minusil-5 was less than 5 μm in diameter and respirable in size.

4. Discussion

Test results indicate that PDM samples can be ashed in less than a day, keeping PDM-oriented quartz analysis in the realm of practicality. Although longer ashing times are required for PDM filter assemblies than for much lighter PVC membranes, the time requirement is still manageable. Options for facilitating large scale analyses include the use of overnight ashing schedules, employing more asher units, or using more efficient ashers to shorten the needed time. When fully ashed, high-mass polymer samples are dispersable in isopropanol, a requirement for P-7 sample handling. Pure polymers show compatibility with the P-7 analytical method when fabricated into forms useful as PDM filter assembly components. LOQ estimates in this research suggest that the current P-7 LOQ will likely be maintained when filters other than typical PVC membranes are employed for sample collection. These results enable some compositional discretion in constructing ashable filters for TEOM use.

Results from analysis of open-face samples suggest that the new formulations for PDM filters have fully addressed the analytical obstacles that existed with the original filter design. The controlled conditions of the experiment reduced potentially confounding factors and focused on the inherent capacity of the new filters to accommodate P-7 analysis of collected quartz. P-7 analytical results were very close to those expected, suggesting that quartz analysis with the novel filter designs can be suitably accurate. For the PDM-collection tests, in which PDM and PVC quartz samples were collected in parallel, compared P-7 results

were very similar. This suggests that the two sampling devices collect quartz particulates in a similar manner. These spectro-metric data also suggest the suitability of ashable PDM filters for quartz analysis and the adaptability of the P-7 method for new filter variations. The gravimetric comparisons for the PDM-collection tests, which show close agreement between PDM and PVC reference filters, further support that PDM instruments and cyclone samplers collect quartz particulates similarly.

PDMs gave EOF readings with modest positive biases compared to gravimetric measurements. The standard deviation for the NIOSH weighing facility for a dust mass determination based on four weighings (*i.e.*, pre- and post-weighings of both a sample and a subtracted blank) is known to be ~8 μg . This is less than 2% of the dust masses in this research. It is prudent to treat EOF bias as real, in that gravimetric error does not appear to be an explanation. Changes in filter design may require recalibration in many cases, but calibration checks with polyester-back filters produced TEOM calibration factors within 1% of those used with standard EMFAB filters. Therefore, altered TEOM calibration does not appear to explain EOF bias.

A variety of significant factors, such as humidity and temperature changes, pressure pulsation, and external vibration, may all impair TEOM accuracy.¹⁶ An additional error,¹⁷ likely related to all PP filters slightly deforming with heat, may cause several μg positive bias over 1–2 h tests. Baseline drift in TEOMs is the result of all error and drift influences added together. Characterization of error and drift effects is beyond the scope of this article, but they may be individually or collectively corrected by modifications in TEOM operation and data processing. All accuracy UCLs for this research are less than 25%, meeting NIOSH criteria, but if accuracy refinement is desired, alterations in instrument operation are possible to address error sources.

Both filter compositions tested are compatible with P-7 analysis, but EOF data comparisons to PDM filter gravimetric measurements showed better accuracy values (Table 1) for polyester-back filters. While achieving quartz analysis with ashable filters has been the primary goal, maintaining PDM mass accuracy is also a consideration, and further work with cellulose-back filters is not recommended. The emergence of a currently preferred filter formulation should not be taken as negating other possible design and application variations, embodying the same concepts and principles of this research. In creating ashable

TEOM filters, quartz analysis of collected dust samples becomes possible, but this initial use does not restrict the range of other applications. Analysis of various other minerals and inorganic materials becomes possible also, through use of appropriate ashing methods. The innovation is not only applicable to the PDM and mining implementations, but also other TEOM types and their related environmental and monitoring applications as well.

5. Conclusions

Through redesign with appropriate materials, PDM filters can be constructed that are fully ashable. Although ashing times are longer than for membrane filters, complete organic matrix destruction of prototype filters can be performed in a low temperature asher. Ashable PDM filters can accommodate P-7 analysis for collected quartz particulates and introduce no problematic infrared interference, if TiO₂ is eliminated from all components. P-7 analysis of polyester-back prototype filters, the currently preferred nylon fiber formulation, results in quartz measurement accuracy within 10% and precision within 4%. This is within the declared 13% accuracy and 7–10% precision of the P-7 analytical method itself. The P-7 method can accommodate changes in the filter analyzed, and ashable PDM filters are a workable variation in sample type. PDMs using polyester-back prototype filters currently show a positive EOF measurement bias ranging within 3–8% when referenced to gravimetric measurements. If desired, instrument programming changes can correct the bias. Continued work with specialized PDM filters is merited, as they are a new type of TEOM sample amenable to ashing analysis of mineral and inorganic particulates. Procedures of Kennedy *et al.*¹³ provide guidelines appropriate for follow-up testing and validation of ashable filter performance in monitoring and analysis. Test variations with mixed composition particulates, as well as field trials, should be included in validation work.

6. Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of NIOSH. Reference to any company name or product does not imply endorsement by NIOSH.

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Implementing infrared determination of quartz particulates on novel filters for a prototype dust monitor

Appendix A. Extended data tables

Table A-1: P-7 analysis of ashed candidate filter assembly materials

Table A-1 reports the results for P-7 sample analysis of candidate materials. Integrated absorbances are recorded for peaks at ~ 915 (930-900) and ~ 800 (815-770) cm^{-1} , used for quantifying kaolin and quartz. Presumed (false) masses of these minerals are also recorded, resulting from calculations with the integrated absorbances. Estimates are given for bias, calculated as the mean of false quartz masses, and limit of quantitation (LOQ), calculated as ten times the root mean square of false quartz masses.

Table A-2: Open-face sample gravimetric and P-7 comparison analyses

Table A-2 records the results of the open-face PDM filter tests. The table reports gravimetrically assessed sample masses and the expected P-7 quartz results, using the 0.942 correction factor. Actual P-7 quartz measurements are also reported for both variations of reference spectra employed, as well as percent deviation of P-7 results from expected values. Data are pooled for each PDM filter type.

Table A-3: P-7 comparison analyses for PDM-collected and PVC filters

Table A-3 records the spectrometric results for the PDM-collection tests. The table reports P-7 measured quartz masses for the prototype PDM filters, the related PVC reference samples, and the percent difference between them. Data are grouped by test run for each PDM filter type. Individual PDM filter results are compared to mean reference filter results.

Tables A-4 and A-5: Gravimetric comparisons for polyester- or cellulose-back and PVC filters from PDM-collection tests

Tables A-4 and A-5 report the sample masses for the PDM-collection tests, based on gravimetric assessment of PVC filters and PDM filters of each type. Again, data are grouped by test run and individual PDM filter results are compared to mean PVC filter results. The tables also report PDM-assessed end-of-file (EOF) dust masses, the final instrument mass reading for each test file. Individual EOF results are compared to mean PVC filter and mean PDM filter gravimetric results. These tables address PDM dust measurement accuracy with the new prototype filters. Results are reported as mass measurements and percent differences for the comparisons made.

Table A-1 P-7 analysis of ashed candidate filter assembly materials

Material tested	Integrated absorbance		Mass/ μg		Bias est. ^c	LOQ est. ^d
	$\sim 915\text{ cm}^{-1}$	$\sim 800\text{ cm}^{-1}$	Kaolin ^a	Quartz ^b		
PVC-acrylic membrane ^e	0.0117	0.0323	0.5	0.6	0.3	4.2
	0.0061	0.0195	0.3	0.4		
	0.0045	-0.0013	0.2	-0.1		
PVC membrane ^e	0.0079	0.0158	0.3	0.3	0.6	6.7
	0.0045	0.0170	0.2	0.3		
	0.0050	0.0613	0.2	1.2		
	0.0010	0.0208	0.0	0.4		
White PP ring/base sets with TiO_2	-0.0422	-0.7812	-1.8	-15.4	-22.5	243.9
	-0.0468	-0.8371	-2.0	-16.5		
	-0.0509	-1.7969	-2.2	-35.7		
Clear PP ring/base sets	0.0091	0.0048	0.4	0.0	0.3	3.3
	0.0121	0.0249	0.5	0.4		
	-0.0056	0.0174	-0.2	0.4		
High wt. PP electret blown melt fiber	-0.0057	-0.0096	-0.2	-0.2	0.0	1.4
	0.0053	0.0061	0.2	0.1		
	0.0073	0.0058	0.3	0.1		
Med. wt. PP electret blown melt fiber	0.0129	-0.0057	0.6	-0.2	0.2	3.1
	0.0088	0.0156	0.4	0.3		
	0.0147	0.0233	0.6	0.4		
Spun bound cover for electret with TiO_2	0.0191	-0.1744	0.8	-3.6	-2.9	29.9
	0.0052	-0.1607	0.2	-3.2		
	0.0067	-0.0921	0.3	-1.9		
Non-woven cover for electret	0.0112	0.0045	0.5	0.0	0.0	0.6
	0.0343	0.0119	1.5	0.0		
	0.0021	-0.0025	0.1	-0.1		
All-nylon fibrous filter	-0.0108	0.0482	-0.5	1.0	1.3	13.7
	-0.0102	0.0368	-0.4	0.8		
	-0.0133	0.0973	-0.6	2.0		
HEPA all-nylon fibrous filter ^f	-0.0299	-0.0124	-1.3	-0.1	0.5	6.5
	0.0460	0.0378	2.0	0.5		
	0.0021	0.0502	0.1	1.0		
Cellulose with melamine binder	0.0084	0.0221	0.4	0.4	0.5	4.8
	0.0086	0.0310	0.4	0.6		
	0.0064	0.0227	0.3	0.4		
High strength cellulose	-0.0012	0.0251	-0.1	0.5	0.2	3.1
	0.0040	0.0096	0.2	0.2		
	-0.0008	0.0000	0.0	0.0		

^a (Kaolin mass in μg) = $(915\text{ cm}^{-1}\text{ integr. abs.})/0.023$ ^b (Quartz mass in μg) = $\{(800\text{ cm}^{-1}\text{ integr. abs.}) - [(915\text{ cm}^{-1}\text{ integr. abs.})/3.62]\}/0.050$ ^c Calculated as mean of quartz mass values. ^d Calculated as 10 x root mean square of quartz mass values.^e Reference filter materials. ^f Most promising new filter material.

Table A-2 Open-face sample gravimetric and P-7 comparison analyses

Sample type	Grav.	0.942 x Grav.	Reference = PVC-acrylic filter		Reference = PVC-acrylic + PDM filters	
	mass/ μ g	mass/ μ g	P-7 mass/ μ g	P-7/Grav. diff. (%)	P-7 mass/ μ g	P-7/Grav. diff. (%)
Polyester-back	529	498	495	-0.7	489	-1.9
	514	484	495	2.2	485	0.2
	514	484	485	0.2	482	-0.5
	512	482	474	-1.7	472	-2.1
	524	494	491	-0.5	489	-0.9
	517	487	496	1.8	492	1.0
	495	466	492	5.5	487	4.4
	498	469	466	-0.7	457	-2.6
	501	472	482	2.1	483	2.3
	513	483	495	2.4	495	2.4
Pooled mean =	511.7	482.0	487.1	1.1	483.1	0.2
Pooled SD =	10.9	10.3	10.3	2.2	11.1	2.3
Cellulose-back	497	468	465	-0.7	467	-0.3
	498	469	461	-1.7	462	-1.5
	491	463	456	-1.4	456	-1.4
	487	459	461	0.5	461	0.5
	539	508	499	-1.7	501	-1.3
	488	460	448	-2.5	449	-2.3
	487	459	460	0.3	459	0.1
	484	456	458	0.5	458	0.5
	490	462	483	4.6	486	5.3
	539	508	504	-0.7	503	-0.9
Pooled mean =	500.0	471.0	469.5	-0.3	470.2	-0.1
Pooled SD =	21.0	19.8	19.1	2.0	19.3	2.1

Table A-3 P-7 comparison analyses for PDM-collected and PVC filters^a

PDM no.	Polyester-back filters			Cellulose-back filters		
	PDM filter P-7 mass/μg	PVC filter P-7 mass/μg	PDM/PVC _M diff. (%)	PDM filter P-7 mass/μg	PVC filter P-7 mass/μg	PDM/PVC _M diff. (%)
		453			445	
1	451	448	0.6	451	434	1.6
2	452	443	0.8	451	441	1.6
3	418	449	-6.7	435	455	-2.0
Mean =	440.3	448.3	-1.8	445.7	443.8	0.4
		458			489	
1	433	474	-5.1	448	476	-4.8
2	462	438	1.2	466	475	-1.0
3	420	456	-8.0	460	443	-2.3
Mean =	438.3	456.5	-4.0	458.0	470.8	-2.7
		454			402	
1	422	448	-6.5	408	419	-0.5
2	447	451	-0.9	417	408	1.6
3	444	452	-1.6	413	412	0.7
Mean =	437.7	451.3	-3.0	412.7	410.3	0.6
		463			430	
1	467	447	3.0	422	452	-3.5
2	466	457	2.8	436	430	-0.3
3	-	447	-	432	438	-1.3
Mean =	466.5	453.5	2.9	430.0	437.5	-1.7
		439			446	
1	413	431	-4.0	443	450	-2.5
2	428	422	-0.5	449	471	-1.2
3	417	428	-3.0	428	450	-5.8
Mean =	419.3	430.0	-2.5	440.0	454.3	-3.1
		431			447	
1	460	469	2.4	432	449	-2.5
2	449	451	0.0	442	440	-0.3
3	445	445	-0.9	446	437	0.6
Mean =	451.3	449.0	0.5	440.0	443.3	-0.7
		Pooled mean =	-1.6		Pooled mean =	-1.2
		Pooled SD =	3.5		Pooled SD =	2.1

^a Subscript M denotes the mean of the sample type indicated.

Table A-4 Gravimetric comparisons for polyester-back and PVC filters from PDM-collection tests^{a,b}

PDM no.	Mass/ μ g			Difference (%)		
	PDM filter grav.	EOF value	PVC filter grav.	PDM/PVC _M	EOF/PVC _M	EOF/PDM _M
			475			
1	495	512	462	5.4	9.1	5.1
2	494	513	467	5.2	9.3	5.3
3	473	-	474	0.7	-	-
Mean =	487.3	512.5	469.5	3.8	9.2	5.2
			482			
1	484	494	491	1.1	3.2	1.5
2	509	533	463	6.3	11.3	9.5
3	467	-	479	-2.5	-	-
Mean =	486.7	513.5	478.8	1.7	7.3	5.5
			471			
1	472	496	456	0.7	5.9	3.3
2	479	499	479	2.2	6.5	3.9
3	490	-	468	4.6	-	-
Mean =	480.3	497.5	468.5	2.5	6.2	3.6
			487			
1	510	521	472	4.7	7.0	2.9
2	503	519	490	3.3	6.6	2.5
3	-	-	499	-	-	-
Mean =	506.5	520.0	487.0	4.0	6.8	2.7
			457			
1	457	463	448	1.0	2.3	1.5
2	463	485	448	2.3	7.2	6.4
3	448	-	457	-1.0	-	-
Mean =	456.0	474.0	452.5	0.8	4.8	3.9
			481			
1	503	510	484	4.5	6.0	3.8
2	491	503	486	2.0	4.5	2.4
3	480	-	474	-0.3	-	-
Mean =	491.3	506.5	481.3	2.1	5.2	3.1
			Pooled mean =	2.4	6.6	4.0
			Pooled SD =	2.5	2.5	2.3

^a Subscript M denotes the mean of the sample type indicated. ^b PDM no. 3 EOF data was not included.

Table A-5 Gravimetric comparisons for cellulose-back and PVC filters from PDM-collection tests^{a,b}

PDM no.	Mass/ μ g		PVC filter grav.	Difference (%)		
	PDM filter grav.	EOF value		PDM/PVC _M	EOF/PVC _M	EOF/PDM _M
			482			
1	469	517	460	-1.6	8.5	9.2
2	476	529	490	-0.1	11.0	11.8
3	475	-	474	-0.3	-	-
Mean =	473.3	523.0	476.5	-0.7	9.8	10.5
			518			
1	468	537	507	-6.1	7.7	12.4
2	489	548	498	-1.9	9.9	14.7
3	476	-	471	-4.5	-	-
Mean =	477.7	542.5	498.5	-4.2	8.8	13.6
			432			
1	426	459	463	-3.9	3.6	7.7
2	426	467	434	-3.9	5.4	9.5
3	427	-	444	-3.7	-	-
Mean =	426.3	463.0	443.3	-3.8	4.5	8.6
			463			
1	455	458	468	-2.0	-1.4	-1.4
2	472	487	458	1.6	4.8	4.8
3	467	-	469	0.5	-	-
Mean =	464.7	472.5	464.5	0.0	1.7	1.7
			475			
1	496	501	469	4.3	5.3	4.1
2	483	495	485	1.5	4.0	2.8
3	465	-	474	-2.3	-	-
Mean =	481.3	498.0	475.8	1.2	4.7	3.5
			477			
1	443	486	464	-5.4	3.8	8.8
2	447	500	467	-4.5	6.8	11.9
3	450	-	465	-3.9	-	-
Mean =	446.7	493.0	468.3	-4.6	5.3	10.4
			Pooled mean =	-2.0	5.8	8.0
			Pooled SD =	2.8	3.3	4.7

^a Subscript M denotes the mean of the sample type indicated. ^b PDM no. 3 EOF data was not included.